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Technical Report No. 9
PREPARATION AND CHARACTERIZATION OF CHROMIUM(III) OXIDE FILMS
BY A NOVEL SPRAY PYROLYSIS METHOD

by
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Conclusions

Solutions of chromium acetylacetonate in acetic acid, in 30% ethanol/water, and in pure ethanol have been evaluated as source materials for the preparation of α - Cr_2O_3 films on silicon substrates. These solutions were nebulized, sprayed onto the substrate, and thermally decomposed. The optimum preparative conditions were determined. High quality, uniform films free of pinholes, comprised of small particles, and with high dc breakdown voltages were obtained from all three solutions. Thus, the relatively inexpensive technique of spray pyrolysis is shown to be an effective alternative to evaporation (1), sputtering (1-3), and MOCVD (4) for the preparation of α - Cr_2O_3 films. However, there were appreciable differences in deposition rate, in crystallinity, in surface morphology, and in density for films prepared from different solutions.

Acknowledgments

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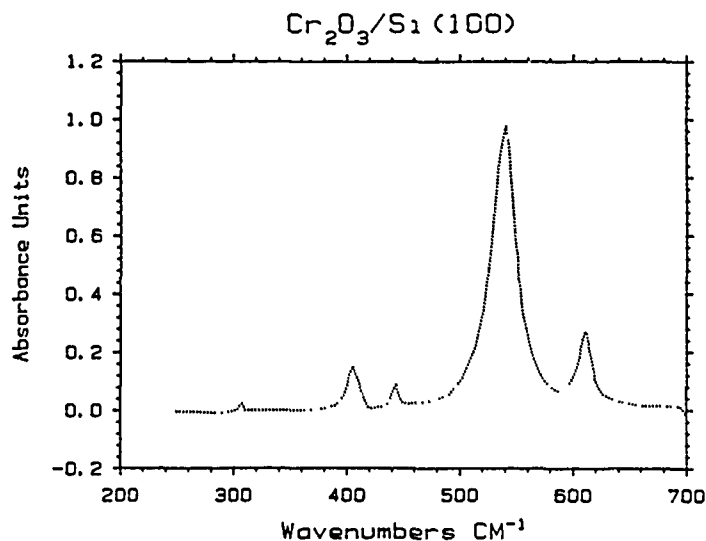


Fig. 3. IR spectra of α -Cr₂O₃ films of 2000 Å thickness.

silicon substrate. Silicon is cubic with $a=5.43\text{\AA}$; α -Cr₂O₃ is hexagonal with $a=4.95\text{\AA}$ and $c=13.58\text{\AA}$. The (110) plane of α -Cr₂O₃ contains the c axis, and 2 times 13.58 gives 27.16 whereas 5 times 5.43 gives 27.15 for silicon. Thus the c -axis of α -Cr₂O₃ is commensurate with the a -axis of silicon, which may be the reason for its preferential growth.

Films prepared from the 30% ethanol/water solutions produced an unusually intense 006 peak in their x-ray patterns. There do not appear to be any obvious correlations between the (001) plane of α -Cr₂O₃ and the (100) plane of silicon to give rise to preferential growth. However, the typical photomicrograph of similar films (Fig. 2b) shows them to consist of acicular particles. It does not seem unreasonable in this case to attribute the modification of normal α -Cr₂O₃ x-ray peak intensities to the shape of the particles. Finally, films prepared from pure ethanol solution produce such broad x-ray peaks that the 104 peak at 33.6° and the 110 peak at 36.2° overlap. This confirms the poor crystallinity inferred above from the particle morphology observed by electron microscopy.

Films of approximately 2000 Å thickness prepared from all three solutions gave the same IR spectra, shown in Fig. 3. This consists of five distinct absorption peaks which are characteristic of α -Cr₂O₃ (12,13).

DC current-voltage measurements were made on films of approximately 2000 Å thickness prepared from all three solutions. No voltage breakdown was observed for potentials up to 20V applied to any of the evaporated gold electrodes. However, films prepared from the 30% ethanol/water solution showed an appreciably greater leakage current (lower resistance) than films prepared from the other solutions. This characteristic may be related to the lower density of these films observed (Fig. 2b) by electron microscopy.



Fig. 2. Electron photomicrographs of $\alpha\text{-Cr}_2\text{O}_3$ films of 2000 Å thickness prepared from: a) 0.005 M $\text{Cr}(\text{acac})_3$ in acetic acid; b) 0.007 M $\text{Cr}(\text{acac})_3$ in 30% ethanol/water; and c) 0.01 M $\text{Cr}(\text{acac})_3$ in ethanol.

used. The spectra of the films were obtained by subtracting the spectra of the uncoated substrates measured prior to film deposition from the corresponding spectra of the coated substrates measured after deposition.

Electrodes for measuring the electrical transport properties of the films were prepared as follows: gold was evaporated through a mask to obtain an array of circular electrodes of area 1.1 mm^2 each on the surface of the chromium(III) oxide film; an indium alloy (Indalloy #9, Indium Corporation of America) was ultrasonically bonded to the back of the silicon substrate. Contact to a gold electrode was made by touching a gold-tipped micromanipulator to the desired spot. The dc current-voltage behavior was measured with the gold positively biased with respect to the substrate and with the reversed polarity.

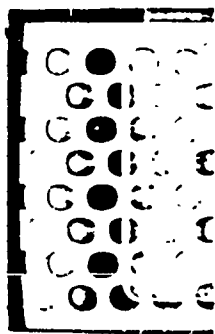
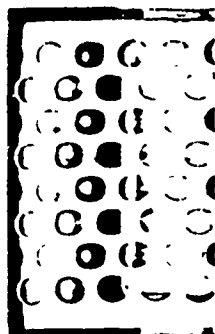
Results and Discussion

Films of chromium(III) oxide of approximately 2000Å thickness have been deposited on silicon by the spray pyrolysis of solutions of chromium acetylacetonate using the conditions given in Table I. However, the time required for the deposition of this standard thickness varies greatly among the three solutions; 8hr for the 0.005M solution in acetic acid, 4hr for the 0.007M solution in 30% ethanol/water, and 2hr for the 0.01M solution in ethanol. For a given solvent, the deposition time would decrease with increasing concentration of $\text{Cr}(\text{acac})_3$. The dramatic observed decrease suggests that the solvent may affect the composition of the complex, and hence its volatility.

The uniformity of the deposited chromium(III) oxide film depends most critically upon the nozzle-to-substrate distance. As shown in Table I, optimum uniformity requires slightly different distances for the three different solutions. The thickness of several films from each solution was measured at different positions with an ellipsometer. For the conditions given in Table I, the thickness of each film was found to be uniform to within 1% except near its very edge. Chromium(III) oxide films of approximately 2000Å thickness are yellow-green in color - the brightness and uniformity of this color confirmed the uniformity of film thickness.

Photomicrographs of 2000Å films prepared from the three solutions are shown in Fig. 2. All three films appear to be homogeneous and free of pinholes, but there are some differences. The film prepared from the acetic acid solution is comprised of densely packed small particles (Fig. 2a) of about 400Å diameter. Their distinct shape indicates appreciable crystallinity. The film prepared from the 30% ethanol/water solution consists of less densely packed, acicular particles (Fig. 2b) of approximately $1000 \times 200 \text{ Å}$. These also show appreciable crystallinity. The films prepared from the pure ethanol solution again consist of densely packed small particles (Fig. 2c) of about 400Å diameter, but their less distinct shape indicates a less crystalline character.

None of the above 2000Å films showed any peaks in their x-ray diffraction patterns. Hence films of 4000Å thickness were similarly prepared. The x-ray diffraction patterns of these thicker films showed only the characteristic peaks of $\alpha\text{-Cr}_2\text{O}_3$, which is consistent with the IR results discussed below. However, films prepared from the acetic acid solution produced an unusually strong 110 peak in their x-ray patterns, which indicates that there has been a (110) preferential growth of $\alpha\text{-Cr}_2\text{O}_3$ on the (100)



reactor by a carrier gas. The nebulized solutions were delivered to the substrate in 5 sec pulses with 15 sec intervals between pulses. The substrates consisted of 1 cm squares of n-type (100) silicon with 8 Ω -cm resistivity. They were cleaned and etched immediately prior to the deposition according to the procedure described by Fournier et al.(10). The reactor was heated by a two-zone mirror furnace (Trans-Temp, Chelsea, MA). Typical sets of reaction parameters for obtaining films of 2000 \AA thickness from the three solutions are given in Table I. Since the carrier gas for the solution of $\text{Cr}(\text{acac})_3$ in pure ethanol was argon (for safety reasons), an additional heating for half an hour at 450 $^\circ$ in oxygen was necessary.

Characterization of films

X-ray diffraction patterns of the films were obtained using a Philips Diffractometer with monochromated high intensity $\text{CuK}\alpha_1$ radiation ($\lambda=1.5404 \text{ \AA}$). Diffraction patterns were taken with a scan rate of $1^\circ 2\theta/\text{min}$ over the range $20^\circ < 2\theta < 70^\circ$.

The thickness of the films was determined by ellipsometry using a Rudolph Research Auto EL-II Ellipsometer. The wavelength of the laser beam was 632.8 nm. The calculation of thickness from the observed data employed the values $N_s=3.877$ and $K_s=0.019$, respectively, for the real and imaginary parts of the index of refraction of the silicon substrates (11).

The surface morphology of the films was examined by means of a JEOL-840F Scanning Electron Microscope (SEM) operating at 4.5 kV.

The IR spectra were obtained using a Bruker IR 98 FTIR Spectrometer with a deuterated triglycine sulphate detector equipped with a polyethylene window. The light source was a Hg arc; 12, 6, and 3.5 μm mylar beamsplitters were

Table I: Reaction Parameters

Spray Solution:	0.005M in 0.66M Acetic Acid	0.007M in 30% Ethanol/water	0.01M in Ethanol
Substrate Temperature	450 $^\circ\text{C}$	450 $^\circ\text{C}$	450 $^\circ\text{C}$
Carrier Gas	Oxygen	Oxygen	Argon
Flow Rate	3.5L/min	3.5L/min	3.5L/min
Nozzle-Substrate Distance	7.3 cm	7.5 cm	8.5 cm
Cycle Time	20 sec	20 sec	20 sec
Nebulization Time	5 sec	5 sec	5 sec
Number of Cycles	1400	600	300

It was the purpose of this work to investigate the preparation and properties of thin $\alpha\text{-Cr}_2\text{O}_3$ films deposited on silicon substrates by this spray pyrolysis method. Various solutions of chromium acetylacetonate were ultrasonically nebulized, sprayed onto silicon substrates, and thermally decomposed at a low temperature. The resulting chromium(III) oxide films were characterized by x-ray diffraction, ellipsometry, scanning electron microscopy, IR spectroscopy, and their electrical transport behavior.

Experimental

Preparation of solutions

Chromium acetylacetonate $\text{Cr}(\text{acac})_3$ was prepared as described in the literature (9). Three different chromium acetylacetonate solutions were used for spray pyrolysis in this investigation: (a) Solutions of 0.005M $\text{Cr}(\text{acac})_3$ in 0.66M acetic acid were prepared by slowly dissolving 0.438g of $\text{Cr}(\text{acac})_3$ in 10 ml of acetic acid in a 250ml volumetric flask which was then filled to volume with distilled water; (b) solutions of 0.007M $\text{Cr}(\text{acac})_3$ in a 30% ethanol/water mixture were prepared by slowly dissolving 0.613g of $\text{Cr}(\text{acac})_3$ in 75ml of ethanol in a 250ml volumetric flask which was then filled to volume with distilled water; (c) solutions of 0.01M $\text{Cr}(\text{acac})_3$ in pure ethanol were prepared by putting 0.875g of $\text{Cr}(\text{acac})_3$ in a 250ml volumetric flask which was then filled to volume with ethanol.

Preparation of films

The above solutions of chromium acetylacetonate were ultrasonically nebulized, sprayed onto silicon substrates, and thermally decomposed at 450° in the reactor shown in Fig. 1. The solutions were nebulized by a commercial ultrasonic humidifier (Holmes Air) and the resulting mist was swept into the

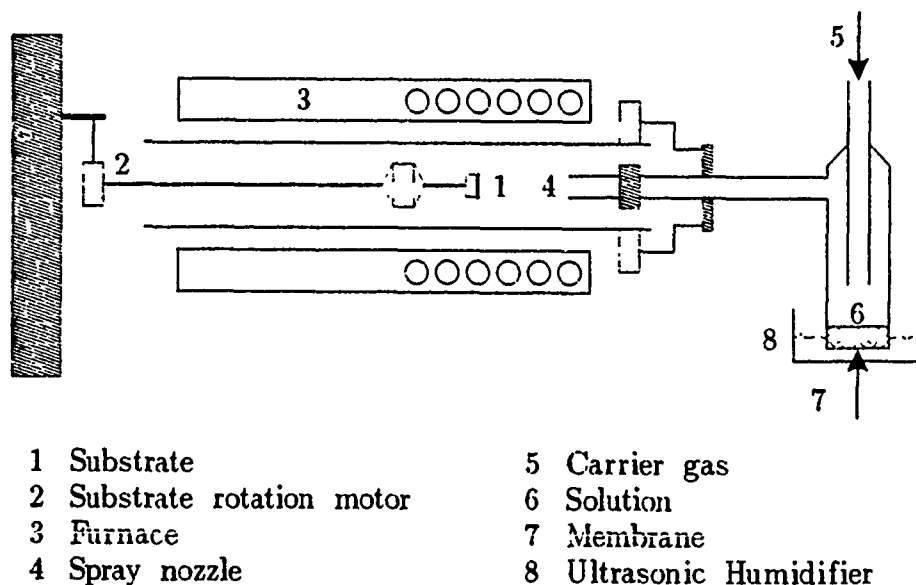


Fig. 1. Spray pyrolysis reactor

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PREPARATION AND CHARACTERIZATION OF CHROMIUM(III) OXIDE FILMS
BY A NOVEL SPRAY PYROLYSIS METHOD

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ABSTRACT

Chromium (III) oxide films of 2000Å thickness were deposited on n-type silicon wafers by a novel spray pyrolysis method. Different spray solutions, all containing a chromium acetylacetonate complex, gave different rates of film deposition. IR spectroscopy of these films confirmed them to be $\alpha\text{-Cr}_2\text{O}_3$. The deposited films of $\alpha\text{-Cr}_2\text{O}_3$ were found to be homogeneous and uniform with breakdown potentials in excess of 20 V. The characteristics of films prepared from different spray solutions are compared and discussed.

MATERIALS INDEX: chromium, oxides, thin films

Introduction

Chromium(III) oxide $\alpha\text{-Cr}_2\text{O}_3$ is a good candidate for thin insulating layers in electronic devices (1). Such films would be useful for numerous applications as protective coatings (2), as well as for isolation masks on the alumina output windows of high-power klystron tubes (3) to prevent damage arising from the high yield of secondary electrons by alumina.

Previous efforts to prepare films of $\alpha\text{-Cr}_2\text{O}_3$ on various substrates have used evaporation (1), sputtering (1,2), magnetron sputtering of metallic chromium followed by oxidation (3), and MOCVD (4). Other low temperature methods for the preparation of films of $\alpha\text{-Cr}_2\text{O}_3$ need to be investigated. Among the alternative methods, spray pyrolysis processing has been shown to be relatively inexpensive and effective for the preparation of oxide films (5). A novel spray pyrolysis process has recently been developed for the preparation of thin oxide films of high quality (6-8).